Dated APR 21, 1998

MEMORANDUM

TO: Diana Love, Director, NEIC

FROM: David Bussard, Director, HWID
Barnes Johnson, Director, EMRAD

SUBJECT: Withdrawal of Cyanide and Sulfide Reactivity Guidance

Thank you for your memorandum of February 18,1998 regarding your concerns about the effectiveness of the Office of Solid Waste's guidance for evaluating potentially reactive cyanide- and sulfide-bearing wastes. These wastes are regulated as characteristically hazardous (waste code D003) at 40 CFR 261.23(a)(5) under a narrative description of reactivity. In July 1985, OSW issued guidance describing a likely mismanagement scenario for cyanide- and sulfide-bearing wastes and providing guidance on "safe" threshold levels for cyanide and sulfide in these wastes in that scenario. The guidance also provided a laboratory method for evaluating these wastes. This guidance was later incorporated into Chapter 7 of SW-846, the Agency's overall guidance document for testing wastes. Your memo expressed serious concerns about the effectiveness of this guidance in evaluating the hazards posed by cyanide- and sulfide-bearing wastes over the full range of likely management scenarios. It also urged OSW to withdraw the guidance.

OSW staff have carefully reviewed and discussed in detail the concerns you raised in your memo and its attachments, and have also reviewed the original guidance mismanagement scenario, derivation of the guidance threshold values, and relation of the scenario and thresholds to the results of the test. After this careful consideration, it is our conclusion that there were critical errors made in developing the guidance, that your concerns regarding the reliability of the guidance are well founded, and that the guidance should be withdrawn. This memo withdraws the July, 1985 guidance. A Federal Register notice announcing the withdrawal of the guidance from SW-846 will be prepared as soon as is feasible.

Your memo raised several concerns about the guidance. These concerns and our replies are:

1. NEIC Concern: The current test does not evaluate waste over the full range of pH values specified in the regulation (pH 2 to 12.5). While the test begins with acid at pH 2, immediately after mixing with the waste, the pH of the mixture may change. It may be somewhere within the range of 2 to 12.5 if the waste does not bear much acidity or alkalinity (due to neutralization or stabilization), but it may not be within this range if the waste does bear substantial acidity or alkalinity. Nevertheless, the test evaluates a single pH condition and not the range of pH conditions (2 to 12.5) specified in the regulations.

   Reply: You are correct, the test will not always be run at the low end of the pH range specified in the regulation (and does not test at the high end of the range). However, the implications and importance of this are not clear, as solubility of the cyanide salts present also affects the rate of conversion to HCN. The addition of a fixed amount of acid with a pH of 2.0 to a waste that may have a substantially higher pH means that when these are mixed, the resulting pH will be higher than pH 2.0. The pH range specified in the regulation was chosen because outside of the pH range 2 to 12.5, the waste acid or base to which the evaluated material is added would be considered a corrosive hazardous waste, and consideration of waste compatibility would be required by 40 CFR 264.17 before the wastes are mixed. This would prevent many dangerous situations from occurring. However, an overwhelming volume of waste acid at pH 2 could be legally added to other wastes, with potentially dangerous effects if the other wastes bear releasable cyanides. In addition, some cyanide salts are much more soluble (and, therefore, more available to react) under high pH conditions; evaluation of hazard under these conditions, as well as at low pHs, should be explored.

2. NEIC Concern: The test and threshold limits presented in the 1985 memo fail to account for Henry's Law, which describes the air-aqueous partitioning of the toxic gases. The result is that the amount of nitrogen used in the test to recover the evolving hydrogen cyanide gas recovers only a small amount of the hydrogen cyanide gas generated. A similar problem, although not as severe, exists for the evolution of hydrogen sulfide gas. Both theoretical calculations and practical tests in our laboratory and other laboratories, demonstrate recoveries in the range of 2% to 3% of the cyanide present. Somewhat higher recoveries are obtained for sulfide, but still not a quantitative recovery.

   Reply: In developing the guidance test, the Agency was not seeking a method that would achieve complete recoveries of hydrogen cyanide and hydrogen sulfide, but rather was attempting to evaluate the risks from wastes in a particular mismanagement scenario. Because hydrogen cyanide is extremely soluble in water, high recovery rates will not be achievable. Henry's Law may be important for assessing hydrogen sulfide, but does not appear to be critical to our judgements about highly soluble gases or to gases that interact with water. This may explain the differences in recovery between hydrogen cyanide and hydrogen sulfide as measured in NEIC tests. We will work with your staff to better understand the role of Henry's Law in the evolution of dissolved HCN gas as we develop revised guidance.

3. NEIC Concern: The test method and the mismanagement scenario are different with respect to air volume, aqueous solution volume, and the amount of waste. According to Henry's Law, this means that toxic gas partitioning between the air and aqueous volumes will be different. The threshold limits fail to account for these differences, and thus are not founded in good science.

   Reply: We have reviewed the original mismanagement scenario and laboratory test conditions, and agree that the conditions (air volume, aqueous solution volume, and waste mass) are different and not correctly scaled between the mismanagement scenario and test (see Attachment 1). There were also several errors made in setting up the calculations in the mismanagement scenario (see Attachments 2 and 3). The fact that these important parameters are mismatched in the laboratory test and the open pit mismanagement scenario means that the test (under these conditions), and the threshold values, do not evaluate the mismanagement scenario conditions. Also, the "dumpster" and "tank" mismanagement scenarios, and your theoretical calculations, described in Attachment II, indicate that the open pit scenario used in the 1985 guidance may not be a true plausible worst case mismanagement/exposure scenario. The Agency clearly needs to consider these alternative mismanagement scenarios as revised guidance is developed.

Until revised guidance is developed, we reiterate the RCRA regulatory language. That is, 40 CFR 261.23(a)(5) specifies that human health and the environment must not be endangered by evolved toxic gases when these wastes are exposed to pH conditions between 2 and 12.5. Any waste causing a hazard, when in the pH range of 2-12.5, would certainly be considered a characteristic hazardous waste.

We understand that withdrawal of the guidance today means that waste generators who have relied on this guidance in the past will, in the near term, have somewhat greater uncertainty about determining the regulatory status of their cyanide- and sulfide-bearing wastes. However, the Agency believes that generators of sulfide- and cyanide-bearing wastes can recognize the acute toxicity of sulfides and cyanides without relying on the test in the guidance. Where wastes with high concentrations of soluble sulfides and cyanides are being managed, generators have relied on their knowledge of the waste to classify them as D003. The Agency expects that generators should continue to classify their high concentration sulfide- and cyanide-bearing wastes as hazardous based on the narrative standard.

Regarding LDR treatment requirements, there are numerical treatment standards for cyanide waste in 40 CFR 268.40 (compliance with these standards is based on different tests than the tests under consideration in this memo; nothing in this memo changes those standards in any way). However, the reactive sulfide treatment standards require that the waste be "deactivated", without specifying numerical treatment standards. Withdrawal of the guidance may leave some generators uncertain about the type and degree of treatment needed to meet the standard for sulfide-bearing wastes. The treatment methods described in 40 CFR 268 Appendix VI, when operated appropriately, can effectively treat sulfide reactive wastes.

Going forward, OSW staff will contact your staff to begin the effort to delete the cyanide and sulfide guidance values and test methodology from Chapter 7 of SW-846. We will also coordinate with your staff to create a working group to explore the development of more specific alternative guidance that relies on: (1) our improved modeling tools for evaluating hazards posed by cyanide- and sulfide-bearing wastes; and (2) better chemical analysis tools for measuring HCN and H_2S release.

Attachments (3)

ATTACHMENT 1: COMPARISON OF CYANIDE/SULFIDE TEST CONDITIONS AND MISMANAGEMENT SCENARIO CONDITIONS

Issue	Treatment in test	Treatment in mismanagement scenario
Air Volume	60 ml/min X 30 min= 1.8L = 0.0018m^3 (Test uses nitrogen flow through enclosed flask)	15m X 1.5m X 4 m= 90m^3 (A fixed block of unmixed air moves across the pit)
Liquid volume	250 ml less waste vol	Not specified in scenario. Approx 15m X 15m X 2.5m=600m^3
Time	30 min X 60 sec/min= 1800 sec	Assumes 10 seconds for a fixed air volume to move across the pit and become contaminated
Mass of waste available to react	10 g waste sample	10% per second of 6130 kg (for 10 seconds)
Total HCN released to cause 10 mg/m^3 HCN	10 mg/m^3 X 0.0018 m^3=0.018 mg HCN	10 mg/m^3 X 90 m^3=900 mg
Ratio air vol/mass waste	0.0018 m^3/0.010 kg=0.18 m^3/kg waste	90 m^3/6130 kg=0.015 m^3/kg waste
Evolution rate of HCN per kg waste present	(0.018mg/1800 sec)/ 0.01 kg waste = 0.001 mg-sec^{-1}/kg waste	(900 mg/10 sec)/6130 kg= 0.015 mg-sec^{-1}/kg waste
Theoretical HCN evolution rate	0.018 mg/1800 sec=1 X 10^{-5}mg/sec	900 mg/10 sec= 90 mg/sec
Total HCN needed to be evolved per kg waste present to cause 10 mg/m^3 HCN	0.018 mg HCN/0.010 kg sample= 1.8 mg HCN/kg waste	900 mg HCN/6130 kg = 0.15 mg HCN/kg waste

ATTACHMENT 2: ANALYSIS OF CALCULATIONS IN JULY 1985 RELEASABLE SULFIDE/CYANIDE GUIDANCE

Calculation presented in mismanagement scenario:

$$R = \text{Guidance threshold level} = \frac{\text{Amount of toxic gas that has to be released/length of test}}{\text{Mass of waste available to release } H_2S \text{ (or HCN)}} \quad (1)$$

Adding values to the calculation:

$$R = \frac{(V)\,(C)\,(1800/10)}{(M/10)} \quad (2)$$

Where: V= the contaminated air volume= 90 m^3
C= air threshold level=10 mg/m^3
1800= Seconds in laboratory test
10 (numerator)= Seconds in mismanagement scenario-- i.e., it takes 10 seconds for the slice of air to move across the pit
M=mass of waste =6130 kg
10=(denominator) percentage of pit area available to contaminate air, per second= 10%-sec^{-1}

Note: Not all values were labeled with units in the guidance memo; assumed units based on information provided in the guidance are: the 1800 seconds, 10 seconds (numerator) and 10%-sec^{-1}(denominator).

$$R = \frac{(90m^3)\,(10\ mg/m^3)\,(1800sec/10sec)}{(6130kg/10\%\text{-}sec^{-1})} \quad (3)$$

R= 264 mg-sec HCN/kg waste (4)

In performing the above calculation, the units fail to cancel to the units of the threshold value of 250 mg/kg waste. There is an extra “seconds” left over which makes the units of the calculation mg-sec/kg waste, a nonsense result.

Also, in moving from the initial form of the calculation (1) to addition of values (2), the equation appears to change. In (1) the total mass of HCN needed to contaminate the air is divided by the length of the test. In (2), the total amount of HCN needed to contaminate the air volume is multiplied by the ratio of the time in the laboratory test to the time it takes the slice of air to move across the pit and become contaminated.

However, the more fundamental error is in introducing time into the equation at all; there are two time errors. The first is in introducing the test time frame (1800 sec) into the mismanagement scenario calculation. This results in an 1800-fold error in the resulting threshold value, and a trailing “seconds” unit. The second time error is in requiring 10% per second of the waste be available to contaminate the $90m^3$ of air as it moves across the pit in 10 seconds. The values and units here cancel out, but there is still the trailing “seconds” from the 1800 seconds on test that results in nonsense units on the answer.

Because the air volume to be contaminated is fixed and unmixed, the only important calculation is the total amount of HCN evolution required to contaminate the $90m^3$ slice of air above the pit. If we want a standard in relation to the amount of waste present, then:

$$R=\frac{(90m^3)\ (10\ mg/m^3)}{6130\ kg\ waste}$$

$$R=0.147\ mg\ HCN/kg\ waste$$

If this result is multiplied by the erroneously included 1800 seconds, the result is 264 mg-sec HCN/kg waste, the incorrect guidance value in the 1985 memo.

The attached table (Attachment 1) shows that this calculated result is unrelated to the laboratory test it was associated with. If we want to relate this result to laboratory test results, additional calculations that correctly scale the static conditions of the mismanagement scenario to static test conditions would be needed. Time (or gas evolution rate) could be added to this guidance value and the laboratory test with additional development work. Developers of the guidance and test apparently believed the rate of gas evolution was important (since they included it in the calculations), they simply included it incorrectly.

However, another significant concern about presenting the guidance in this form (i.e., mg HCN/kg waste) is that the guidance value is totally dependent on the waste volume (and air volume) used. A tenfold change in the waste volume or static air volume results in a tenfold change in the guidance threshold, a clearly unsatisfactory result. Revised guidance will need to incorporate the need to consider mismanagement scenarios different from the one presented in the guidance.

Mismanagement scenario:

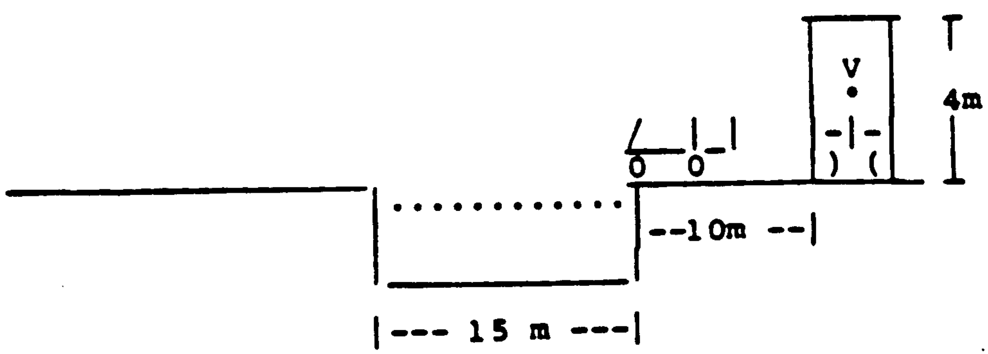
A truckload of waste is discharged into a pit containing acidic waste. As a result of the reaction of the waste with the acid, a rapid, high level release of toxic gas ensues. The objective of the characteristic is to identify those wastes which, if such an activity were to take place, pose a hazard to those persons in the general vicinity fo the disposal site.

Assume:

1. The truckload of waste contains 6130 kg of waste (about a 5 yd^3 dump truck @ 100 lbs/ft^3).
2. The velocity of the wind is 150 cm/sec (3.4 mph).
3. A person is standing 10 meters from the edge of the disposal pit.
4. Exposure to concentrations of:
   HCN above 10 mg/m^3 or
   H_2S above 20 mg/m^3
   pose an acute, immediate danger to human health.
5. The area of the pit over which the toxic gas is generated covers 225 m^2.
6. Before reaching an exposed individual the plume of contaminated air disperses, in a linear manner, to a height of 4 meters.

Then:

1. The minimum toxic gas release rate that would have to be present to exceed the danger level can be calculated using the following model.



2. Total Available Toxicant level then that poses a hazard can be calculated as follows:

V is a hypothetical volume of air to which an individual is exposed. Since the pit is 15 meters wide, and V is assumed to be 1.5 m thick, V = 15 m wide x 4 m high x 1.5 m thick = 90 m^3

is the time it takes for a given volume of air to travel across the surface of the pit and become contaminated with toxic gas. Since the wind speed is

150 cm/sec, and the volume slice is assumed to be 1.5 m thick, T = 10 seconds

C is concentration in mg/m^3 of toxicant that poses a danger.

A is the amount of toxicant contained in V when V is contaminated to a level that poses a health hazard. A = V x C. Since a given "slice" of air takes 10 seconds to move across the pit, this amount of toxicant can be generated over 10 seconds.

M is mass of waste dumped into the pit.

R is the total available toxicant necessary to pose a hazard as measured using the attached test protocol.

$$= \frac{\text{Amount of toxic gas that has to be released/length of test}}{\text{Mass of waste available to release } H_2S}$$

$$= \frac{(A)(1800/T)}{\text{(M/Percent of pit area available to contaminate air volume in any given unit of time)}}$$

$$= \frac{(V)(C)(1800/T)}{(M/10)}$$

$$= \frac{(90)(C)(1800/10)}{(6130/10)}$$

$$= \frac{(90)(C)(180)}{(613)}$$

= 26.4 (C)

= 264 mg/Kg total available cyanide

= 528 mg/Kg total available sulfide

3. As an added margin of safety, we accordingly recommend the action levels of:

Total Available Cyanide: 250 mg HCN/Kg waste
Total Available Sulfide: 500 mg H_2S/Kg waste